X-ray Fluoresence Analysis of Trace Metals in Solvent Refined Coal

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Introduction

This work was undertaken to ascertain the ability of Energy Dispersive X-ray Fluoresence (EDXRF) analysis to determine trace element content of Solvent Refined Coal (SRC). As a result of recent improvements in the design of solid state detectors for X-ray Fluoresence it is now possible to do very rapid simultaneous quantitative analysis of a large number of elements. In this work some 17 elements are quantitatively analyzed in both raw feed coal and product SRC from the Wilsonville SRC Pilot Plant, Wilsonville, Alabama.

The content of trace metals in SRC product and in feed coal is important for several reasons: Certain metals, particularly iron, catalyze the hydrogenation and hydrodesulfurization reactions that occur in the SRC process. If the SRC product is to be used to fire a gas turbine, then trace metals such as Ca, Na, and V present potential corrosion or fouling problems. When the feed coal has a high oxygen and a low sulfur content, a substantial portion of western, sub-bituminous coal, for example, has a low sulfur (~0.7%) and a high oxygen (~17%) content, trace metals such as Ca react with CO_2 formed in the SRC dissolver and tend to collect in the dissolver, eventually resulting in plugging problems. Trace metals such as As in SRC product present potential environmental problems. Also, metals such as Fe and Al are present in sufficient quantity in the feed coal that the SRC mineral residue represents an attractive source of these metals when current sources have been depleted.

Analysis of trace elements in coal has been the subject of many earlier papers (1,2,3). In fact, analytical methods, specifically, atomic absorption, (4,5) have been presented for determining the content of trace metals in clean coal products such as SRC product. However, because of the large number of analyses required to maintain reasonable quality control of SRC product, etc., alternative methods that are hopefully more rapid and less expensive than those currently available are needed. Application of EDXRF to perform assays of feed coals and SRC products is attractive because it allows simultaneous analysis of trace elements found in feed coals and SRC products. This work demonstrates that EDXRF is an effective method for determining the content of trace metals in coal and coal-derived products.

Experimental

Equipment

All EDXRF analyses were done on a Kevex 0810RW X-ray Fluoresence System (Kevex Corporation, Burlingame, Ca. 94010) consisting of a 0810A X-ray Subsystem, 5100C analyzer, 5100 X-ray Spectrometer Rigaku Gigerflex 3kW X-ray generator, (60 kV and 180 ma) Digital Electronics Corporation PDP 11/03 Computer with RX01 dual floppy disk bulk storage. The system uses a high power X-ray tube (Ag target) to produce X-rays from a series of selectable secondary targets (Ti, Ge, Mo, and Sn). The spectrometer uses a solid state detector of 30 mm^2 active area that has resolution of <165eV @ 1KHz.

Atomic Absorption experiments for iron were done on a Perkin-Elmer Model 305A Atomic Absorption spectrophotometer (Perkin-Elmer Corporation, Norwalk, Connecticut 06856) using an acetylene/air flame and a wavelength setting of 249 nm. Sulfur determinations were made using a Leco model 521-500 sulfur analyzer specially fitted for low level sulfur detection (Laboratory Equipment Corporation, St. Joseph, Michigan 49085).

Procedure

Approximately 10 g. samples of all coals and SRC's were first ground so that the entire sample passed through a 325 mesh screen. The samples were then dried in a vacuum oven at 105°C for at least 3 hours. From these samples 1.25 inch pellets were made using a boric acid backing and were analyzed by EDXRF under a vacuum of 5×10^{-4} torr. Also, fractions of the same samples were used to perform Leco sulfur, C, H and N, and Atomic Absorption analyses.

The raw EDXRF data were analyzed using the Kevex matrix correction program, and adaptation of the shell EXACT (6) program. The EXACT program employs a fundamental parametric method which accounts for matrix interactions due to absorption and enhancement for all the elements in the sample. The EXACT model is basically similar to models presented by Sherman (7), Shiraiwa (8) and Criss and Birks (9) with simplifications.

Results

Table 1 gives a comparison between EDXRF and two methods, Atomic Absorption (AA) and Leco, commonly used in this laboratory for analysis of iron and sulfur, respectively. At the bottom of Table 1 are analyses for three standards (Certified Atomic Absorption Standard, 1000 ppm iron, Fisher Scientific, FairLawn, New Jersey 07410; Calibration Standard no. 764-547 (2.02 ± 0.03% S) and Calibration Standard no. 764-545 (0.31 ± 0.02% S) LECO Corporation, 3000 Lakeview, St. Joseph, Michigan 49085). These standards were purchased for use in calibration of atomic absorption and LECO analysis. In all cases EDXRF gave the best accuracy for the standards analysis.

Table 2 gives the EDXRF elemental analyses for 12 coals and SRC's. As expected smaller amounts of the 17 elements analyzed for were detected in the SRC products than in the respective feed coals.

Little would actually be gained by an element by element comparison of the various coals and SRC's. On the other hand, Figure 1 gives an interesting correlation between ash content of moisture free coal and cumulative weight percent of 15 elements (Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, and Sr) as determined by EDXRF. Least Squares analysis of the data gave a straight line correlation factor (r) of 0.92 at the 95% confidence level. An r value of 0.92 indicates a reasonable fit was obtained and that the resulting correlation can be used to compute the approximate percent ash in feed coals. Most importantly, these data demonstrate that the ash content of a feed coal can be approximated very rapidly in this manner. At this time experiments are in progress to show that the same relationship is also true for SRC product.

Summary and Conclusion

It has been shown that EDXRF is capable of analyzing coals and SRC's for elemental content. These analyses provide simultaneous results for several important elements, namely sulfur, iron and calcium, as well as percent ash. These analyses presently take well over 2 hours per sample to complete, but by using EDXRF this time can be reduced to less than one hour per sample. Furthermore, EDXRF has an added feature in that it may be automated, leading to even shorter analysis times per sample. Thus, EDXRF can be concluded to be an effective tool that can provide very accurate and rapid analyses of coals and SRC product for their elemental content.

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TABLE 1

Comparison of EDXRF to Atomic Absorption and Leco Sulfur

Coal	XRF	A.A.	Leco	Known Value
Western Kentucky				
Fe	0.697	0.800		
S	2.24		2.56	
Wyodak				
Fe	0.265	0.247		
S	0.637		0.764	
Illinois #6				
Fe	0.629	0.526		
S	2.76		2.45	
Pittsburg #8				
Fe	0.561	0.615		
S	2.22		2.87	
Monterrey				
Fe	1.165	0.732		
S	3.07		3.24	
Rosebud				
Fe	0.466	0.270		
S	0.976		1.04	
Bighorn				
Fe	0.267	0.216		
S	0.582		0.620	
Standards				
Fe	0.1072	0.937		0.1000
S	1.995		2.22	2.02
S	0.301		0.278	0.31

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TABLE 2

EDXRF Analysis of SRC and Coal

Element	A	B	wt.% C	D	E	F
Si		1.612		1.813		2.097
P	0.0755	0.183	0.0657	0.186	0.0840	0.251
S	0.723	2.24	1.04	2.22	0.755	2.76
Cl	0.0097	0.0177	0.0053	0.105		
K	0.001	0.0977		0.100		0.112
Ca	0.0087	0.0817	0.0144	0.910	0.0024	0.148
Ti	0.0092	0.0383	0.0088	0.0537	0.0178	0.0549
V	0.0037	0.0089	0.0049	0.0099	0.0036	0.0149
Cr		0.0036	0.0026	0.0025	0.0023	0.0058
Mn	0.0018	0.0022	0.0008	0.0043	0.0026	0.0048
Fe	0.0427	0.697	0.0191	0.561	0.0199	0.629
Ni	0.0002	0.0010	0.0008	0.0038	0.0010	0.0020
Cu	0.0003	0.0012	0.0006	0.0028	0.0014	0.0017
Zn	0.0005	0.0013	0.0007	0.0038	0.0006	0.0015
As	0.0001	0.0008	0.0002	0.0005	0.0001	0.0006
Br	0.0002	0.0003	0.0004	0.0009	0.0003	0.0005
Sr		0.0014		0.0132		0.0014

A Western Kentucky SRC
B Western Kentucky 9/14 Coal
C Pittsburg #8 SRC
D Pittsburg #8 Coal
E Illinois #6 SRC
F Illinois #6 Coal

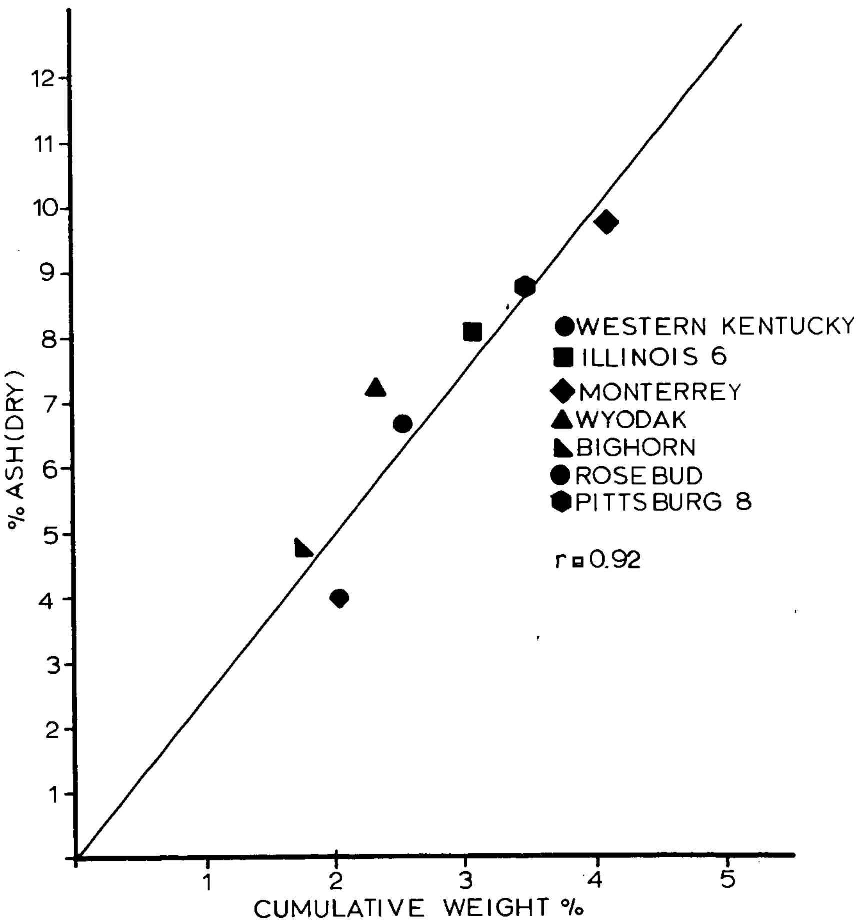
TABLE 2 CONTINUED

EDXRF Analysis of SRC and Coal

Element	G	H	I	J	K	L
			wt.%			
Si		1.073	0.1021	2.578	0.821	0.903
P	0.0306	0.143	0.0953	0.2193	0.122	0.101
S	0.152	0.6371	1.172	3.070	0.976	0.582
Cl	0.0036	0.0536		0.241	0.106	
K		0.0310	0.0040	0.1245	0.0266	0.0204
Ca	0.0162	0.858	0.0022	0.2750	0.557	0.473
Ti	0.0078	0.0585	0.0133	0.0617	0.0352	0.0511
V	0.0023	0.0353	0.0034	0.0104	0.0124	
Cr	0.0017	0.0033		0.0090	0.0110	0.0041
Mn	0.0012	0.0031		0.0087	0.0063	0.0025
Fe	0.0228	0.2615	0.0450	0.1651	0.466	0.2667
Ni	0.0013	0.0006		0.0015	0.0019	0.0014
Cu	0.0017	0.0056	0.0010	0.0201	0.0017	0.0058
Zn	0.0005	0.0020	0.0004	0.0016	0.0004	0.0013
As	0.0001	0.0004	0.0001	0.0006	0.0003	0.0005
Br		0.0002	0.0004	0.0005	0.0008	0.0001
Sr	0.0001	0.0137	0.0007	0.0013	0.0088	0.0074

G Wyodak (Amax) SRC
H Wyodak (Amax) Coal
I Illinois (Monterrey) SRC
J Illinois (Monterrey) Coal
K Rosebud Coal
L Big Horn Coal

FIGURE 1


12
11
10
9
8
7
6
5
4
3
2
1
% ASH(DRY)
1
2
3
4
5
CUMULATIVE WEIGHT %
WESTERN KENTUCKY
ILLINOIS 6
MONTERREY
WYODAK
BIGHORN
ROSEBUD
PITTSBURG 8
r = 0.92